Frontiers in Mechanochemistry and Mechanical Alloying
© CSIR-National Metallurgical Laboratory, Jamshedpur-831007, India, 2011

INCOME2008
1-4 December, 2008

MECHANICAL ALLOYING OF Al-C SYSTEM

Michal Besterci[1ξ], Katarína Sülleiová[1], Oksana Velgosová[2]
[1]Institute of Materials Research of Slovak Academy of Sciences, Kosice, Slovak Republic,
[2]Technical University of Kosice, Metallurgical faculty, Kosice, Slovak Republic

Keywords: Aluminium-graphite powder system, Mechanical alloying, Carbon to Al_4C_3 transformation, Microstructure, Mechanical properties

Abstract

A method of mechanical alloying process is described. Carbon transformation to Al_4C_3 is characterised within the different heat treatment schedules and nine commercial carbon powders are tested. The micromechanism of carbon incorporation into the metallic powder, and its compacting are described. The influence of dispersed carbides on mechanical properties is evaluated together with the influence of deformation on microstructure and properties.

It was proved that the transformation efficiency of carbon to Al_4C_3 by heat treatment of aluminium with the porous furnace black and electrographite is higher than that of the hard cracked graphite. Microstructure changes consisted of fracture processes and welding of the particles with incorporation of C phase and forming of final granules. The dispersed phase Al_4C_3 particle size was measured on 200 to 300 thin foil structures, and it was constant and as small as 30 nm. The particle size was influenced neither by the carbon type nor by the heat treatment applied. Subgrain size measured in the range of 100 grains in thin foils depended on the carbon type, as well. It ranged from 0.3 to 0.7 µm. Using a depth sensing indentation (DSI) technique, the Martens hardness, indentation modulus E and deformation work W for Al matrix and Al_4C_3 particles have been measured. It has been shown that the hardness of particles is 5–7 times higher than the hardness of the matrix. The temperature dependence of ductility, and reduction of area in the temperature range of 350 – 450°C and strain rate of 10^{-1} s^{-1}, indicated a considerable increase of these properties. In a case when the volume fraction of Al_4C_3 changes from lower to higher, the grain rotation mechanism dominates instead of the grain boundary sliding.

Introduction

The mechanical alloying was first developed and used to prepare superalloys with a nickel matrix, and the method spread to other alloys later. Dispersoids can be formed in a solid state reaction by introducing materials that react with the matrix in the time following heat treatment [1,2]. A mode of mechanical alloying is reaction milling, developed for dispersion strengthened aluminium production [3,4]. The aim of this paper is to study the influence of the various graphite types (when mixed with Al powder) and heat treatment procedure on the microstructure and properties of dispersion strengthened aluminium alloys in the system Al-Al_4C_3.

Materials and Methods

The experimental material - dispersion strengthened aluminium with Al_4C_3 particles, was prepared by intense milling of aluminium powder with different types of carbon, as shown in Table 1. The prime aluminium powder grain size was 100 m with the carbon content of 0.6 - 3 wt.%.

Table 1. Different types of carbon used in the study

Notation	Type	Commercial Carbon	Notation	Type	Commercial Carbon
A	a_1	LTD	F	a_2	Farbruss FW 2
B	a_1	Spezialschwarz 5	G	a_2	Flammruss 101
C	a_1	Spezialschwarz 500	H	c	Thermax
D	a_1	Printex 30	I	b	Grafit KS 2.5
E	a_2	Printex 400			

The aluminium composite dispersion strengthened by Al_4C_3 particles has been prepared by the method of mechanical alloying. The milling time used in all tested specimens was 90 min. The final carbide content was in the range of 2.5-12 vol.%. The obtained mixture was compacted at 600 MPa and heat treated at 450, 500, 550, and 600°C whereas treatment times of 1, 3, 10, and 30 hours were employed. The final compacting by hot extrusion at a temperature of 550°C and a reduction of 94% in the cross circular section of extruded bars was applied [5]. The experimental material - has been both prepared, and tested by gas chromatography for carbides Al_4C_3 content, at the Institute for Chemical Technology of Inorganic Materials, TU Vienna.

Results and Discussion

Milling and Carbonisation Kinetics

Figure 1 shows the milling kinetics, the effect of milling time on the dislocation density and subgrain size of the matrix. After milling for 120 min these parameters are constant, [6]. From the results, it can be inferred that the homogeneity of carbide distribution and contact surface area influence the kinetics of transformation of Al+C to Al_4C_3. The dependence of the transformation rate on temperature and holding time for the four carbon types is shown in Fig. 2. The good susceptibility to

ξ email: mbesterci@imr.saske.sk

transformation for porous furnace black (a_1 and a_2) and that of electro-graphite (b) is evident. The porous carbon types are incorporated into the matrix by friction during milling, the distribution is uniform, and clustering is small. On the other side, hard graphite (c) resists disintegration and the granules are large.

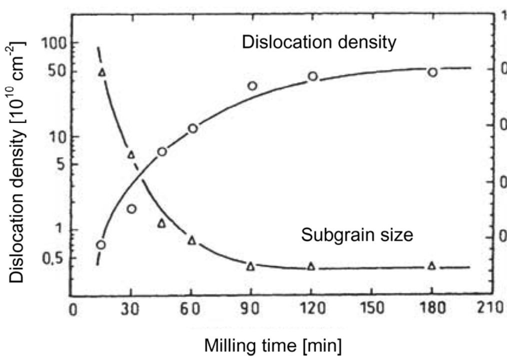

Figure 1. Dislocation density and subgrain size in Al +1 mass-% C milled granulate, as a function of the milling time

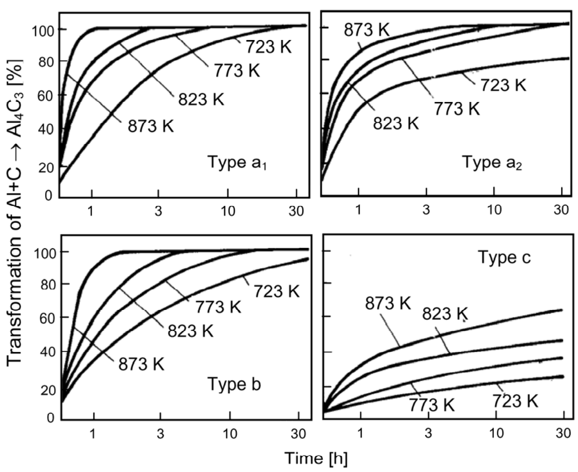

Figure 2. Dependence of carbon to the carbide transformation rate on heat treatment temperature and holding time for four carbon types

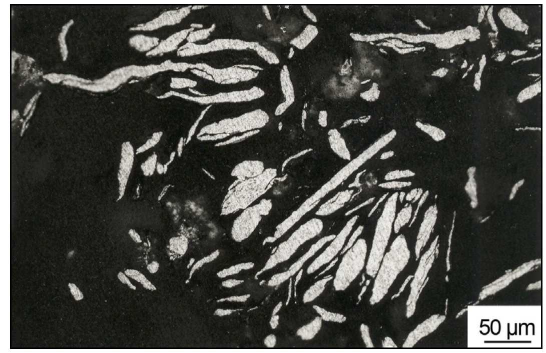

Figure 3. State of granules after 10 mim milling of Al + 1C material

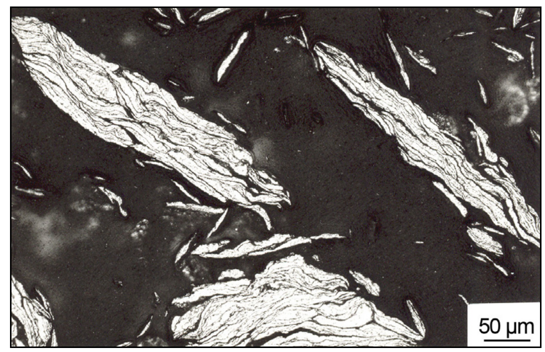

Figure 4. Granules after 30 min milling - welding process, Al+1C material

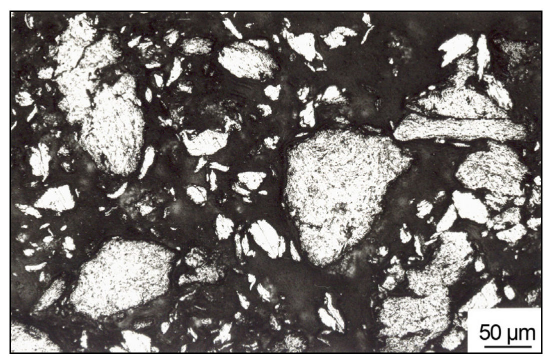

Figure 5. State of granules after 60 min milling, Al + 1C material

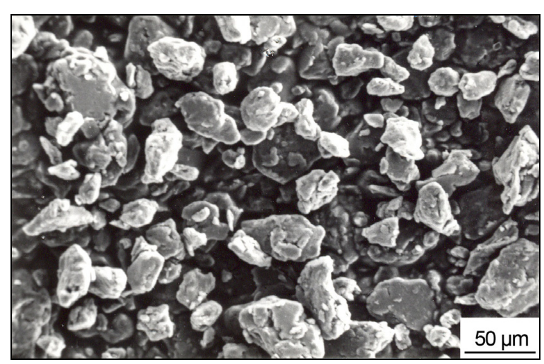

Figure 6. Shape of granules after 240 min milling of Al + 1C material

Microstructure and Mechanical Properties

Light microscopy microstructure analysis of the produced compacts proved a high homogeneity of dispersed particle distribution in the direction perpendicular to the direction of hot extrusion. In the longitudinal direction of the bar as a result of hot extrusion the Al_4C_3 carbide particles were arranged into bands.
Milling mechanism of Al-1C system from the time point of view is shown in Figs. 3-6. Microstructure changes occurred in the fracture processes and welding of the particles with incorporation of C phase and forming of final granules.

Electron microscopy analysis was conducted using carbon replicas and thin foils. TEM of thin foils offered better results. For all the tested carbon combinations from the A to I labels, thin foils were produced for the heat treatment 450°C/30 h. The Al_4C_3

particle size and the subgrain size were measured using the thin foils. The dispersed phase Al_4C_3 particle size was measured on 200 to 300 thin foil structures, and it was constant and as small as 30 nm. The particle size was influenced neither by the carbon type nor by the heat treatment applied. Subgrain size measured in the range of 100 grains in thin foils depended on the carbon type, as well. It ranged from 0.3 to 0.7 μm. The stability of properties, resulting from graphite type I (KS 2.5), led to the highest production and utilization of this type of dispersion strengthening, [7].

In our previous works [8-10], we have evaluated the distance between the particles by point object simulation methods. This includes the mean interparticle distance λ_{μ}, the mean minimum distance λ_{ρ}, the mean visibility λ_{ν}, and the mean free spherical contact distance λ_{ϑ}. The characteristics and properties of these parameters have been analyzed in [9]. Schematic illustration of interparticle distance is shown in Fig. 7.

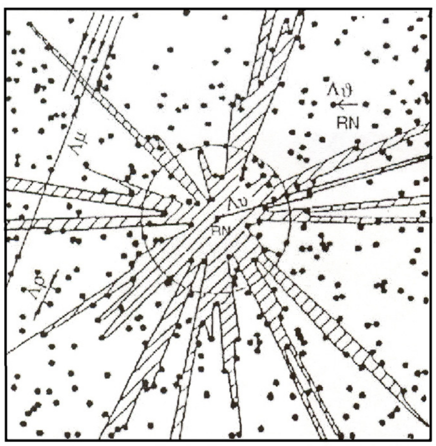

Figure 7. Schematic illustration of interparticle distance

During the last years, a new approach to the description of point systems has been developed intensively, which is referred to as polygonal methods [10]. The dual representation formed in the above way describes completely the given point system. Properties of Voronoi tessellation and their various generalizations are being very intensively studied now and the state of this study is given in the monograph [11]. Intermediate stages of evaluation for thin foil (a), outlines of particles (b), and of reference points (c) are documented in Fig. 8.

The Al-Al_4C_3 system with 4 vol. % of Al_4C_3 was tested under different tensile conditions, where three different strain rates and different testing temperatures up to 450°C were used [12-13]. The results are shown in Fig. 9. The deformation mechanism and fracture mechanism were analysed corresponding to different testing conditions. For the higher strain rates of $10^{-1}s^{-1}$ at 450°C, a significant growth of plastic properties was observed. The high uniform elongation A_5 of the specimen gauge length, and corresponding reduction values of the reduction in area Z were manifested in Fig. 10. The ductility anomalies are showing an onset of a type of superplasticity. According to [14-16] it was proved that for materials Al - $12Al_4C_3$, the main mechanism responsible for superplastic behaviour is the grains rotation process and not sliding.

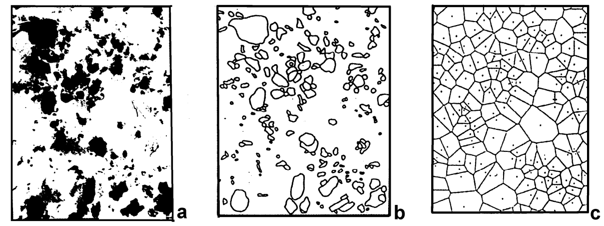

Figure 8. Intermediate stages of evaluation for this foil (a), outlines of particles (b) and reference points (c)

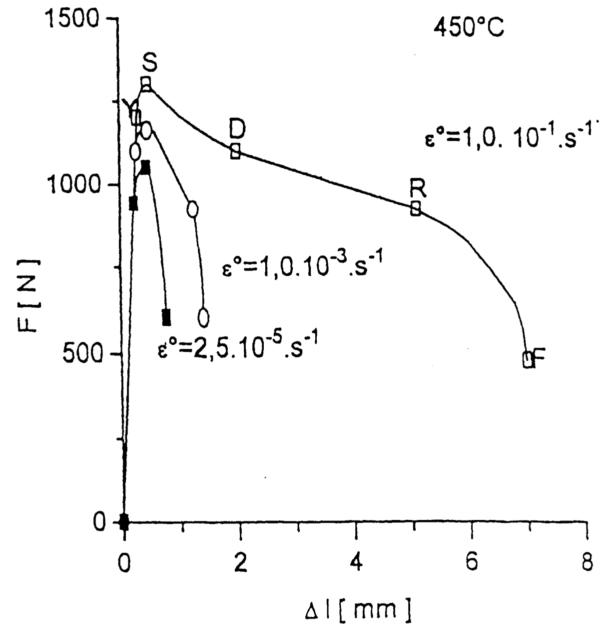

Figure 9. Stress-strain dependences at 450°C

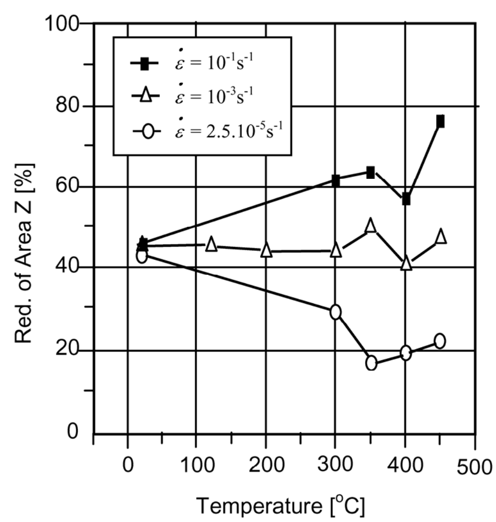

Figure 10. Reduction of area Z as a function of strain rate and temperature

The comparison of real F- Δl curves for material Al-Al_4C_3 with 12% Al_4C_3 is given in Fig. 11. In the curves for 20 and 300°C the first part with deformation strengthening is followed immediately by the loss of plastic stability, plastic deformation localization and fracture. On the other side curves for high strain rate and temperatures of 400 and 450°C showed after part *I*, a definitely linear part *II* with near constant true stress, sometimes called 'plateau', with dynamic recovery, and only after that the part (*III*), with the loss of plastic stability.

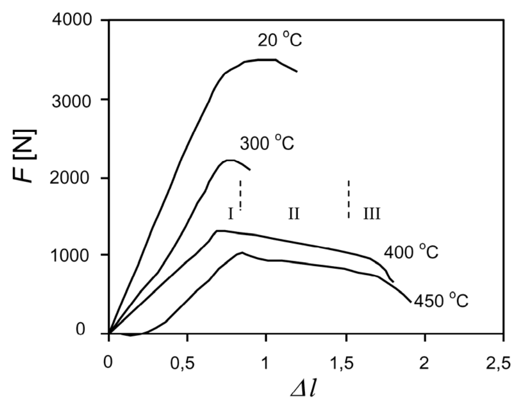

Figure 11. Comparison of real F-Δl curves of the composite materials Al-Al_4C_3 for temperatures from 20 to 450°C and strain rate of $10^{-1}s^{-1}$

The plastic properties are expressed by ductility A_5 in Fig. 12 for different Al_4C_3 contents. For low strain rates a decrease of plastic properties is characteristic with the increase of temperature up to 450°C. The increase of the dispersed phase particles content from 4 to 12% decreased the ductility and the reduction of area, too. A peak like significant increase of plastic properties is visible at 400 and 450 °C in all plots (Fig. 12) for the highest strain rate ($\dot{\varepsilon}$) = $1\cdot10^{-1}$ s^{-1}. According to our experience, ductility A_5 is influenced by differences of deformation, and fracture in part *III* of the test. Cut-outs and thin foil TEM micrographs were produced also from the fracture area. The total values of ductility and reduction of area are much lower than those for known superplastic materials.

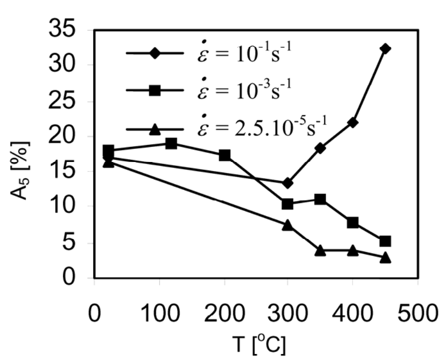

Figure 12. Dependence of ductility on temperature and strain rate for material Al-4Al_4C_3

According to our previous results as well as those described in references, it appears that the deformation in the present Al-Al_4C_3 system includes and combines the following mechanisms:

a) dynamic polygonization by dislocation migration and annihilations,
b) slip on grain boundaries,
c) displacement of grains by rotation,
d) partial recrystallization causing grain boundary movement of polygonized grains,
e) dislocation creep, causing accommodations of defects on grain boundaries (first in ternary points).

Grains can move or be reordered as shown in Fig. 13 by two mechanisms: a) slip along grain boundaries, b) rotation.

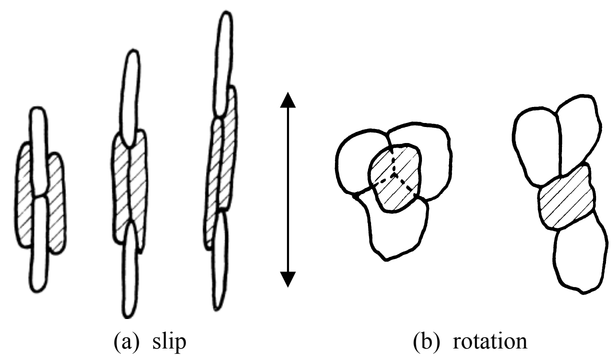

Figure 13. Proposed reordering mechanisms: a) slip; b) rotation

We have analyzed the partial contributions of different mechanisms to the total superplastic deformation. We suppose that at high strain rate ($1\cdot10^{-1}$ s^{-1}) and high dispersed phase content (12 vol.% of Al_4C_3) dynamic recovery is started by the high accumulated deformation energy, then dynamic polygonization of grains, repositioning by rotation (no elongated grains seen), partial recrystallization and dislocation creep can take place, too. Clusters of particles identified as Al_4C_3 in Fig. 14 on grain boundaries suggested more rotation than slip. For low dispersed phase particle content (4 vol.% of Al_4C_3) the elongated grains and slip on grain boundaries are more frequent, with lower probability of polygonization and partial recrystallization Fig. 15.

During deformation of samples with high dispersed phase content at high strain rate, the recovery is not as perfect as known for superplastic materials. Local deformation with neck formation and fracture with limited reduction of area are the signs showing the limits of these materials. We suggest to characterize more precisely the deformation process in the Al-Al_4C_3 system in terms of quasi-superplastic behaviour.

Conclusions

The results can be summarized as follows:

1. It was shown that the transformation efficiency of carbon to Al_4C_3 by heat treatment of aluminium with the porous furnace black *a)* and electrographite *b)* is higher, than that of the hard cracked graphite *c)*.

Figure 14. Substructure (foil) of Al-12Al_4C_3 material – transversal direction

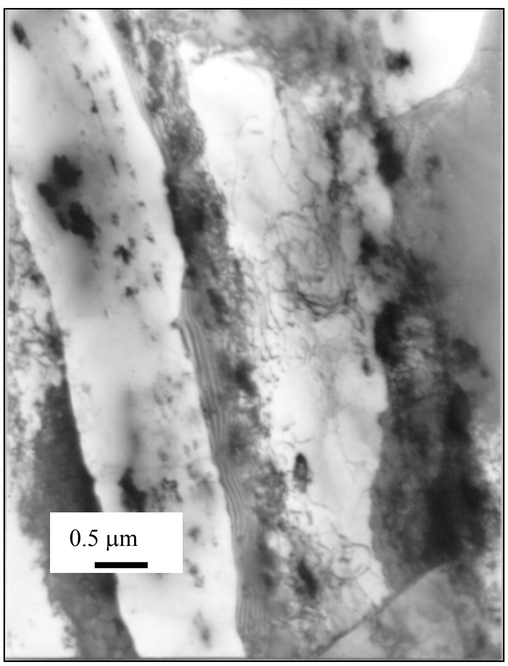

Figure 15. Substructure (foil) of Al-4Al_4C_3 material – longitudinal direction

2. Microstructure changes occurred in the fracture processes and welding of the particles with incorporation of C phase and forming of final granules.
3. The dispersed phase Al_4C_3 particle size was measured on 200 to 300 thin foil structures, and it was constant and as small as 30 nm. The particle size was influenced neither by the carbon type nor by the heat treatment technology applied. Subgrain size measured in the range of 100 grains in thin foils depended on the carbon type, as well. It ranged from 0.3 to 0.7 μm.
4. The temperature dependencies of ductility, and reduction of area in temperature range of 350–450°C and strain rate of 10^{-1} s^{-1}, indicated a considerable increase of these properties.

If the volume fraction of Al_4C_3 changes from lower to higher values, the grain rotation mechanism dominates instead of the grain boundary sliding.

Acknowledgements

This work was supported by Slovak Grant Agency for Science VEGA, project No. 2/0105/08 and the Slovak Research and Development Agency (Project No. APVV-20-027205).

References

1. M. Besterci, *Dispersion strengthened Al prepared by mechanical alloying,* Cambridge, Int. Science Publ., ISBN 189832655 (1999).
2. T. Weissgäerber and B. Kieback, *Materials Science Forum, 8* (2000) 275.
3. G. Korb, G. Jangg and F. Kutner, *Draht,* 30 (1975)318.
4. G. Jangg, F. Kutner and G. Korb, *Aluminium,* 51 (1957) 641.
5. M. Besterci, M. Šlesár, G. Jangg, M. Miškovičová and J. Ďurišin, *Kovové mat*., 27(1) (1989) 77.
6. G. Jangg, M. Šlesár, M. Besterci and J. Zbiral, *Zeischrift f. Werkstofftechnik,* 20 (1989) 226.
7. M. Besterci, *Materials and Design,* 27 (2006) 416 .
8. I. Saxl, M. Besterci, and K. Pelikán, *Pokroky práškové metalurgie* 3 (1986).
9. I. Saxl, K. Pelikán, J. Rataj and M. Besterci, *Quantification and Modelling of Heterogenous Systems,* Cambridge Int. Publication. ISBN 1898326045 (1995).
10. M. Besterci, I. Kohútek, I. Saxl, and K. Sülleiová, *J. of Materials Science,* 34 (1999) 1055.
11. A. Okabe, B. Boots and K. Sugihara, *Spatial Tessellation,* Chichester, John Wiley (1992).
12. M. Besterci, J. Zrník and M. Šlesár, *Kovové mater.,* 35 (1997) 344.
13. M. Besterci, O. Velgosová, J. Ivan and L. Kováč, *Kovové mater.,* 39 (2001) 309.
14. R.S. Mishra and A.K. Mukherjee, *Mater. Sci. Eng*. A, 234-236 (1997) 1023.
15. K. Higashi, *Mater. Sci. and Eng.,* A 166 (1993) 109.
16. M. Besterci, O. Velgosová, L. Kováč and J. Ivan, *Materials Sci. Forum,* 416-418 (2003).207.